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# DETERGENT COSMETIC COMPOSITIONS AND USE

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The present invention relates to novel cosmetic compositions with improved properties intended simultaneously for cleaning and conditioning the hair and comprising, in a cosmetically acceptable vehicle, a washing base composed of surfactants with a detergent power, in which base are also present, as conditioning agents, cationic polymers in combination with a specific amine-comprising silicone. The invention also 10 relates to the use of the said compositions in the abovementioned cosmetic application.

The use of detergent compositions (or shampoos) based essentially on conventional surfaceactive agents of, in particular, anionic, non-ionic 15 and/or amphoteric type but more particularly of anionic type is commonplace in the cleaning and/or washing of hair. These compositions are applied to wet hair and the foam generated by massaging or rubbing with the hands makes it possible, after rinsing with water, to remove the varied dirt initially present in the hair.

These base compositions certainly possess a good washing power but the intrinsic cosmetic properties which are attached thereto however remain fairly weak, in particular due to the fact that the 25 relatively aggressive nature of such a cleaning treatment can in the long term cause more or less marked damage to the capillary fibre, related in

particular to the gradual removal of the lipids or proteins present in or at the surface of the latter.

Thus, in order to improve the cosmetic properties of the above detergent compositions and more particularly of those which are required to be applied to sensitive hair (i.e. hair which is damaged or embrittled, in particular under the chemical action of atmospheric agents and/or of hair treatments, such as permanent waves, dyeings or bleachings), it is now usual to introduce, into the latter, additional cosmetic agents, known as conditioning agents, intended mainly to repair or restrict the harmful or undesirable effects induced by the various treatments or attacks which capillary fibres are more or less repeatedly subjected to. These conditioning agents can, of course, also improve the cosmetic behaviour of natural hair.

The conditioning agents which are most commonly used currently in shampoos are cationic polymers, silicones and/or silicone derivatives,

20 because these confer, on washed, dry or wet hair, an ease of disentangling, a softness and a sleekness which are increased with respect to that which can be obtained with the corresponding cleaning compositions which are devoid of them. In addition, it is known to preferably use a mixture of silicone and of cationic polymer on sensitive hair.

However, and despite the progress recently made in the field of shampoos based on cationic

polymers and on silicone, these are not really completely satisfactory.

This is because the abovementioned cosmetic advantages are unfortunately also accompanied, on dried hair, by certain cosmetic effects which are considered to be undesirable, namely lankness of the hairstyle (lack of lightness of the hair), lack of sleekness (individual hair nonhomogeneous from the root to the tip) and insufficient sheen.

- In addition, the use of cationic polymers for this purpose exhibits various disadvantages. Due to their strong affinity for hair, some of these polymers are deposited to a significant extent during repeated use and result in undesirable effects, such as an
- 15 unpleasant and heavy feel, stiffening of the hair and interfibre adhesion, affecting the styling. These disadvantages are accentuated in the case of fine hair, which lacks liveliness and body.

Thus, a strong need still currently exists

20 with regard to being able to have available novel

products exhibiting a better performance with regard to

one or more of the cosmetic properties mentioned above.

The present invention is targeted at overcoming these disadvantages.

25 Thus, following significant research carried out on the subject, it has now been found by the Applicant Company, entirely unexpectedly and surprisingly, that by using a specific and suitably

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selected amine-comprising silicone as defined below in detergent compositions comprising conventional cationic polymers as conditioning agents, it is possible to limit, indeed even eliminate, the problems generally related to the use of such compositions, namely, in particular, lankness and lack of sleekness and of softness of the hair, while retaining the other advantageous cosmetic properties which are attached to compositions based on conditioning agents, in particular their good intrinsic washing power.

The compositions in accordance with the invention confer on hair, after rinsing, a notable treating effect which is expressed in particular by an ease of disentangling as well as a contribution of body, of lightness, of sleekness, of softness and of suppleness.

All these discoveries form the basis of the present invention.

Thus, according to the present invention,

20 novel detergent and conditioning compositions are now
provided comprising, in a cosmetically acceptable
medium, (A) a washing base and (B) a conditioning
system comprising at least one cationic polymer and at
least one amine-comprising silicone with a weight
25 average molecular mass of between 11,000 and 25,000.

Another subject-matter of the invention is the use in cosmetics of the above compositions for

cleaning and conditioning keratinous substances, in particular the hair.

However, other characteristics, aspects and advantages of the invention will become still more clearly apparent on reading the description which follows and the concrete but in no way limiting examples intended to illustrate it.

As indicated above, the essential components entering into the composition of the products according to the invention are (A) a washing base and (B) a conditioning system comprising (i) the cationic polymer or polymers and (ii) the specific amine-comprising silicone or silicones.

#### 15 A - WASHING BASE:

The compositions in accordance with the invention necessarily comprise a washing base, generally an aqueous washing base.

The surfactant or surfactants forming the
20 washing base can be chosen without distinction, alone
or as mixtures, from anionic, amphoteric, non-ionic,
zwitterionic and cationic surfactants.

However, according to the invention, the washing base preferably comprises anionic surfactants

or mixtures of anionic surfactants and of amphoteric surfactants and, more preferentially still, comprises only this type of surfactant or mixture of surfactants.

The minimum amount of washing base is that just sufficient to confer a satisfactory foaming and/or detergent power on the final composition, and excessively large amounts of washing base do not really contribute additional advantages.

Thus, according to the invention, the washing base can represent from 4% to 50% by weight, preferably from 8% to 35% by weight and more preferentially still from 10% to 25% by weight of the total weight of the final composition.

The surfactants which are suitable for implementing the present invention are in particular the following:

## (i) Anionic surfactant(s):

Their nature does not assume a really critical character within the context of the present invention.

Thus, by way of example of anionic surfactants that can be used, alone or [lacuna]

20 mixtures, in the context of the present invention, there may be mentioned in particular (non-limiting list) the salts (in particular alkali metal, especially sodium, salts, ammonium salts, amine salts, aminoalcohol salts or magnesium salts) of the following compounds: alkyl sulphates, alkyl ether sulphates, alkylamido ether sulphates, alkylarylpolyether sulphates, monoglyceride sulphates; alkylsulphonates, alkyl phosphates, alkylamidesulphonates, alkylaryl-

sulphonates, α-olefinsulphonates, paraffinsulphonates; alkyl sulphosuccinates, alkyl ether sulphosuccinates, alkylamidesulphosuccinates; alkyl sulphosuccinamates; alkyl sulphoacetates; alkyl ether phosphates;

- 5 acylsarcosinates; acylisethionates and N-acyltaurates, the alkyl or acyl radical of all these different compounds preferably comprising from 12 to 20 carbon atoms, and the aryl radical preferably denoting a phenyl or benzyl group. Among the anionic surfactants
- which are further usable, there may also be mentioned the salts of fatty acids, such as the salts of oleic, ricinoleic, palmitic and stearic acids, the acids of copra oil or of hydrogenated copra oil, and acyllactylates in which the acyl radical comprises 8 to
- 20 carbon atoms. It is also possible to use weakly anionic surfactants, like alkyl-D-galactosideuronic acids and salts thereof, as well as polyoxyalkylenated ether carboxylic acids and salts thereof, in particular those comprising from 2 to 50 ethylene oxide groups,
- and mixtures thereof. The anionic surfactants of the polyoxyalkylenated ether carboxylic acid or salt type are in particular those which correspond to the following formula (1):

$$R_1 - (OC_2H_4)_n - OCH_2COOA$$
 (1)

25 in which:

 $R_1$  denotes an alkyl or alkaryl group and n is an integer or decimal number (mean value) which can vary from 2 to 24 and preferably from 3 to 10, the alkyl radical

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having between 6 and 20 carbon atoms approximately and aryl preferably denoting phenyl,

A denotes H, ammonium, Na, K, Li, Mg or a monoethanolamine or triethanolamine residue. Use may also be made of mixtures of compounds of formula (1), in particular mixtures in which the R<sub>1</sub> groups are different.

Among the anionic surfactants, it is preferable to use, according to the invention, alkyl sulphate and alkyl ether suphate salts and mixtures 10 thereof.

## (ii) Non-ionic surfactant(s):

The non-ionic surface-active agents themselves are also compounds which are well known per se (in this respect see in particular the "Handbook of Surfactants" by M.R. Porter, published by Blackie & Son (Glasgow and London), 1991, pp. 116-178) and, in the context of the present invention, their nature does not assume any critical character. They can thus be chosen especially from (non-limiting list) fatty alcohols, alpha-diols, alkylphenols or acids which are polyethoxylated, polypropoxylated or polyglycerolated, having a fatty chain comprising, for example, 8 to 18 carbon atoms, it being possible for the number of 25 ethylene oxide or propylene oxide groups to range especially from 2 to 50 and it being possible for the number of glycerol groups to range especially from 2 to 30. Mention may also be made of the copolymers of

ethylene and propylene oxide and the condensates of ethylene and propylene oxide with fatty alcohols; the polyethoxylated fatty amides preferably having from 2 to 30 mol of ethylene oxide, the polyglycerolated fatty amides on average comprising 1 to 5 glycerol groups and in particular 1.5 to 4; the polyethoxylated fatty amines preferably having 2 to 30 mol of ethylene oxide; the oxyethylenated esters of sorbitan fatty acids having from 2 to 30 mol of ethylene oxide; the sucrose 10 esters of fatty acids, the polyethylene glycol esters of fatty acids, alkylpolyglycosides, the N-alkylglucamine derivatives, or amine oxides, such as the oxides of  $(C_{10}-C_{14})$  alkylamines or the N-acylaminopropylmorpholine oxides. It will be noted that alkylpolyglycosides constitute non-ionic surfactants which enter particularly well into the scope of the present invention.

# (iii Amphoteric or zwitterionic surfactant(s):

20 The amphoteric or zwitterionic surface-active agents, the nature of which does not assume any critical character in the context of the present invention, may be especially (non-limiting list) derivatives of aliphatic secondary or tertiary amines 25 in which the aliphatic radical is a linear or branched chain comprising 8 to 18 carbon atoms and comprising at least one water-solubilizing anionic group (for example carboxylate, sulphonate, sulphate, phosphate or

phosphonate);  $(C_8-C_{20})$  alkyl betaines, sulphobetaines,  $(C_8-C_{20})$  alkyl amido  $(C_1-C_6)$  alkyl betaines or  $(C_8-C_{20})$  alkyl amido  $(C_1-C_6)$  alkyl sulphobetaines may further be mentioned.

- Among the amine derivatives, there may be mentioned products sold under the name Miranol, as described in Patents US-2,528,378 and US-2,781,354 and classified in the CTFA dictionary, 3rd edition, 1982, under the names Amphocarboxyglycinates and
- 10 Amphocarboxypropionates with respective structures:

$$R_2$$
-CONHCH<sub>2</sub>CH<sub>2</sub>-N( $R_3$ )( $R_4$ )(CH<sub>2</sub>COO<sup>-</sup>) (2)

in which:  $R_2$  denotes an alkyl radical of an acid  $R_2$ -COOH present in hydrolysed copra oil, a heptyl, nonyl or undecyl radical,  $R_3$  denotes a beta-hydroxyethyl group and  $R_4$  a carboxymethyl group; and

$$R_2 \cdot -CONHCH_2CH_2 - N(B)(C)$$
 (3)

20 in which:

B represents  $-CH_2CH_2OX'$ , C represents  $-(CH_2)_z-Y'$ , with z=1 or 2,

X' denotes the  $-CH_2CH_2-COOH$  group or a hydrogen atom
25 Y' denotes -COOH or the radical  $-CH_2-CHOH-SO_3H$   $R_2$  denotes an alkyl radical of an acid  $R_9-COOH$  present in copra oil or in hydrolysed linseed oil, an alkyl

radical, in particular  $C_7$ ,  $C_9$ ,  $C_{11}$  or  $C_{13}$ , a  $C_{17}$  alkyl radical and its iso form or an unsaturated radical  $C_{17}$ .

By way of example, there may be mentioned the cocoamphocarboxyglycinate sold under the trade name

5 Miranol C2M concentrated by the Company Miranol.

# (iv) Cationic surfactants:

Among the cationic surfactants, there may be mentioned in particular (non-limiting list): the salts of optionally polyoxyalkylenated primary, secondary or tertiary fatty amines; quaternary ammonium salts, such as tetraalkylammonium, alkylamidoalkyltrialkylammonium, trialkylbenzylammonium, trialkylhydroxyalkylammonium or alkylpyridinium chlorides or bromides; imidazoline derivatives; or amine oxides of cationic nature.

of which is not ruled out, do not constitute preferred surfactants for making use of the present invention.

#### B - CONDITIONING SYSTEM

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## (i) Cationic polymer(s)

The compositions according to the invention, in addition, necessarily comprise a cationic polymer.

The conditioning agents of cationic polymer

25 type which can be used in accordance with the present
invention can be chosen from all those already known
per se as improving the cosmetic properties of hair
treated with detergent compositions, namely, in

particular, those disclosed in Patent Application EP-A 0,337,354 and in French Patent Applications FR-A-2,270,846, 2,383,660, 2,598,611, 2,470,596 and 2,519,863.

More generally still, within the meaning of the present invention, the expression "cationic polymer" denotes any polymer comprising cationic groups and/or groups which can be ionized to cationic groups.

The preferred cationic polymers are chosen

10 from those which comprise units comprising primary,
secondary, tertiary and/or quaternary amine groups,
which can either form part of the main polymer chain or
be carried by a side substituent directly connected to
the latter.

The cationic polymers used generally have a number [lacuna] molecular mass of between 500 and 5  $\times$  10<sup>6</sup> approximately and preferably of between 10<sup>3</sup> and 3  $\times$  10<sup>6</sup> approximately.

Mention may more particularly be made, among cationic polymers, of quaternized proteins (or protein hydrolysates) and polymers of the polyamine, polyaminoamide and poly(quaternary ammonium) type.

These are known products.

The quaternized proteins or protein

25 hydrolysates are in particular chemically modified polypeptides carrying quaternary ammonium groups at the chain end or grafted onto the chain. Their molecular mass can vary, for example, from 1500 to 10,000 and in

particular from 2000 to 5000 approximately. Mention may in particular be made, among these compounds, of:

- collagen hydrolysates carrying triethylammonium groups, such as the products sold under the name "Quat-5 Pro E" by the Company Maybrook and called, in the CTFA dictionary, "Triethonium Hydrolyzed Collagen Ethosulphate";
- collagen hydrolysates carrying trimethylammonium and trimethylstearylammonium chloride groups, sold 10 under the name of "Quat-Pro S" by the Company Maybrook and called, in the CTFA dictionary, "Steartrimonium Hydrolyzed Collagen";
- animal protein hydrolysates carrying trimethylbenzylammonium groups, such as the products sold under the name "Crotein BTA" by the Company Croda and called, in the CTFA dictionary, "Benzyltrimonium Hydrolysed Animal Protein";
  - protein hydrolysates carrying, on a polypeptide chain, quaternary ammonium groups comprising at least one alkyl radical having from 1 to 18 carbon atoms.
    - Mention may be made, among these protein hydrolysates, inter alia, of:
    - "Croquat $^{\otimes}$  L", the quaternary ammonium groups of which comprise a  $C_{12}$  alkyl group;
- 25 "Croquat $^{\otimes}$  M", the quaternary ammonium groups of which comprise  $C_{10}-C_{18}$  alkyl groups;
  - "Croquat $^{\otimes}$  S", the quaternary ammonium groups of which comprise a  $C_{18}$  alkyl group;

- "Crotein® Q", the quaternary ammonium groups of which comprise at least one alkyl group having from 1 to 18 carbon atoms.

These various products are sold by the 5 Company Croda.

Other quaternized proteins or hydrolysates are, for example, those corresponding to the formula:

$$R_{5} = \bigcap_{\text{CH}_{3}}^{\text{CH}_{3}} R_{6} = NH - A \times \Theta$$
(II)

in which X<sup>-</sup> is an anion of an organic or inorganic acid,

10 A denotes a protein residue derived from collagen
protein hydrolysates, R<sub>5</sub> denotes a lipophilic group
comprising up to 30 carbon atoms and R<sub>6</sub> represents an
alkylene group having 1 to 6 carbon atoms. Mention may
be made, for example, of the products sold by the

15 Company Inolex under the name "Lexein® QX 3000", called
"Cocotrimonium Collagen Hydrolysate" in the CTFA
dictionary.

Mention may also be made of quaternized plant proteins, such as wheat, maize or soya proteins:

20 mention may be made, as quaternized wheat proteins, of those sold by the Company Croda under the names "Hydrotriticum WQ or QM", called "Cocodimonium Hydrolysed Wheat Protein" in the CTFA dictionary, "Hydrotriticum QL", called "Laurdimonium Hydrolysed Wheat Protein" in the CTFA dictionary or "Hydrotriticum

QS", called "Steardimonium Hydrolysed Wheat Protein" in the CTFA dictionary.

The polymers of the polyamine, polyamidoamide or poly(quaternary ammonium) type which can be used in accordance with the present invention which can be mentioned in particular are those disclosed in French Patents No. 2,505,348 or 2,542,997. Mention may be made, among these polymers, of:

(1) optionally quaternized vinylpyrrolidone/dialkylaminoalkyl acrylate or methacrylate copolymers, such as
the products sold under the name "Gafquat" by the
Company ISP, such as, for example, Gafquat® 734, 755 or
HS100, or else the product "Copolymer 937". These
polymers are disclosed in detail in French Patents

15 2,077,143 and 2,393,573.

- (2) cellulose ether derivatives comprising quaternary ammonium groups disclosed in French Patent 1,492,597 and in particular the polymers sold under the names "JR $^{\otimes}$ " (JR $^{\otimes}$  400, JR $^{\otimes}$  125, JR $^{\otimes}$  30M) or "LR $^{\otimes}$ " (LR $^{\otimes}$  400,
- 20 LR® 30M) by the Company Union Carbide Corporation.

  These polymers are also defined in the CTFA dictionary as quaternary ammoniums of hydroxyethylcellulose which has reacted with an epoxide substituted by a trimethylammonium group.
- 25 (3) cationic cellulose derivatives, such as the copolymers of cellulose or the cellulose derivatives grafted with a water-soluble quaternary ammonium monomer and disclosed in particular in Patent US

4,131,576, such as hydroxyalkyl celluloses, for example hydroxymethyl-, hydroxyethyl- or hydroxypropyl celluloses, grafted in particular with a methacryloylethyltrimethylammonium, methacrylmidopropyltrimethylammonium or diallyldimethylammonium salt.

The marketed products corresponding to this definition are more particularly the products sold under the name "Celquat<sup>®</sup> L 200" and "Celquat<sup>®</sup> H 100" by the Company National Starch.

- (4) the cationic polysaccharides disclosed more particularly in Patents US 3,589,578 and 4,031,307, such as guar gums comprising cationic trialkylammonium groups. Use is made, for example, of guar gum modified by a 2,3-epoxypropyltrimethylammonium salt (for example, chloride).
  - Such products are sold in particular under the trade names of Jaguar  $^{\otimes}$  C13 S, Jaguar  $^{\otimes}$  C 15, Jaguar  $^{\otimes}$  C 17 or Jaguar  $^{\otimes}$  C162 by the Company Meyhall.
- (5) polymers composed of piperazinyl units and of divalent, straight- or branched-chain alkylene or hydroxyalkylene radicals, optionally interrupted by oxygen, sulphur or nitrogen atoms or by aromatic or heterocyclic rings, as well as the oxidation and/or
- quaternization products of these polymers. Such polymers are disclosed in particular in French Patents 2,162,025 and 2,280,361.

- (6) water-soluble polyaminoamides prepared in particular by polycondensation of an acidic compound with a polyamine; these polyaminoamides can be crosslinked by an epihalohydrin, a diepoxide, a
- dianhydride, an unsaturated dianhydride, a bisunsaturated derivative, a bishalohydrin, a bisazetidinium, a bishaloacyldiamine or an alkyl bishalide or alternatively by an oligomer resulting from the reaction of a bifunctional compound reactive
- with respect to a bishalohydrin, a bisazetidinium, a bishaloacyldiamine, an alkyl bishalide, an epilhalohydrin, a diepoxide or a bisunsaturated derivative; the crosslinking agent being used in proportions ranging from 0.025 to 0.35 mol per amine
- group of the polymaoamide; these polyaminoamides can be alkylated or, if they comprise one or more tertiary amine functional groups, quaternized. Such polymers are disclosed in particular in French Patents 2,252,840 and 2,368,508.
- 20 (7) polyaminoamide derivatives resulting from the condensation of polyalkylenepolyamines with polycarboxylic acids, followed by an alkylation by bifunctional agents. Mention may be made, for example, of adipic acid/diakylaminohydroxyalkyldialylenetriamine
- polymers in which the alkyl radical comprises from 1 to 4 carbon atoms and preferably denotes methyl, ethyl or propyl. Such polymers are disclosed in particular in French Patent 1,583,363.

Mention may more particularly be made, among these derivatives, of the adipic acid/dimethylamino-hydroxypropyl/diethylenetriamine polymers sold under the name "Cartaretine® F, F4 or F8" by the Company Sandoz.

- (8) polymers obtained by reaction of a polyalkylene-polyamine comprising two primary amine groups and at least one secondary amine group with a dicarboxylic acid chosen from diglycolic acid and saturated
- aliphatic dicarboxylic acids having from 3 to 8 carbon atoms. The molar ratio of polyalkylenepolylamine to dicarboxylic acid being between 0.8:1 and 1.4:1; the polyaminoamide resulting therefrom being brought to react with epichlorohydrin in a molar ratio of
- epichlorohydrin in relation to the secondary amine group of the polyaminoamide of between 0.5:1 and 1.8:1. Such polymers are disclosed in particular in United States Patents 3,227,615 and 2,961,347.

Polymers of this type are in particular sold 20 under the name "Hercosett<sup>®</sup> 57" by the Company Hercules Inc. or else under the name of "PD 170" or "Delsette<sup>®</sup> 101" by the Company Hercules in the case of the adipic acid/epoxypropyl/diethylenetriamine copolymer.

(9) cyclohomopolymers of methyldiallylamine or of 25 dimethyldiallylammonium, such as the homopolymers or copolymers comprising, as main constituent of the chain, units corresponding to the formulae (VI) or (VI'):

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$$-(CH_{2})t-CR_{12} -(CH_{2})k$$

$$-(CH_{2})t-CR_{12} -(CH_{2})$$

in which formulae k and t are equal to 0 or 1, the sum k + t being equal to 1;  $R_{12}$  denotes a hydrogen atom or a methyl radical;  $R_{10}$  and  $R_{11}$ , independently of one 5 another, denote an alkyl group having from 1 to 22 carbon atoms, a hydroxyalkyl group in which the alkyl group preferably has 1 to 5 carbon atoms or a lower

amidoalkyl group or  $R_{10}$  and  $R_{11}$  can denote, jointly with

10 heterocyclic group, such as piperidinyl or morpholinyl; Y is an anion, such as bromide, chloride, acetate, borate, citrate, tartrate, bisulphate, bisulphite, sulphate or phosphate. These polymers are disclosed in particular in French Patent 2,080,759 and in its Certificate of Addition 2,190,406.

the nitrogen atom to which they are attached,

- Mention may more particularly be made, among the polymers defined above, of homopolymers of diallydimethylammonium chloride with a number-average molecular mass (Mn) of between 5000 and 200,000 and more particularly with an Mn of between 6000 and 20,000.
- (10) the quaternary diammonium polymer comprising repeat units corresponding to the formula:

$$\begin{array}{c|c}
R_{13} & R_{15} \\
\hline
N+ & A_1 & N+ & B_1 \\
\hline
X- & R_{16} & X-
\end{array}$$
(V11)

in which formula (VII):

R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub> and R<sub>16</sub>, which are identical or different, represent aliphatic, alicyclic or arylaliphatic

5 radicals comprising from 1 to 20 carbon atoms or lower hydroxyalkyl aliphatic radicals or else R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub> and R<sub>16</sub>, together or separately, form, with the nitrogen atoms to which they are attached, heterocycles optionally comprising a second heteroatom other than

10 nitrogen or else R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub> and R<sub>16</sub> represent a linear or branched C<sub>1</sub>-6 alkyl radical substituted by a nitrile, ester, acyl, amide or -CO-O-R<sub>17</sub>-D or -CO-NH-R<sub>17</sub>-D group, where R<sub>17</sub> is an alkylene and D a quaternary ammonium group;

Al and Bl represent polymethylene groups comprising from 2 to 20 carbon atoms which can be linear or branched and saturated or unsaturated, and which can comprise, bonded to or inserted into the main chain, one or more aromatic rings or one or more oxygen or sulphur atoms or sulphoxide, sulphone, disulphide, amino, alkylamino, hydroxyl, quaternary ammonium, ureido, amide or ester groups, and

 $X^{-}$  denotes an anion derived from an inorganic or organic acid;

A1,  $R_{13}$  and  $R_{15}$  can form, with the two nitrogen atoms to which they are attached, a piperazine ring; in addition, if A1 denotes a linear or branched, saturated or unsaturated alkylene or hydroxyalkylene radical, B1 can also denote a  $(CH_2)n-CO-D-OC-(CH_2)n-group$ 

in which D denotes:

- a) a glycol residue of formula: -O-Z-O-, where Z denotes a linear or branched hydrocarbon-comprising radical or a group corresponding to one of the following formulae:
  - $-(CH_2-CH_2-O) \times -CH_2-CH_2-$ 
    - $-[CH_2-CH(CH_3)-O]_v-CH_2-CH(CH_3)-$

where x and y denote an integer from 1 to 4, representing a defined and unique degree of

- 15 polymerization, or any number from 1 to 4 representing a mean degree of polymerization;
  - b) a bis-secondary diamine residue, such as a piperazine derivative;
    - c) a bisprimary diamine residue of formula:
- 20 -NH-Y-NH-, where Y denotes a linear or branched hydrocarbon-comprising radical or else the divalent radical

$$-CH_2-CH_2-S-S-CH_2-CH_2-;$$

d) a ureylene group of formula: -NH-CO-NH-;

Preferably, X is an anion, such as chloride or bromide.

These polymers have a number-average molecular mass generally of between 1000 and 100,000.

Polymers of this type are disclosed in particular in French Patents 2,320,330, 2,270,846, 2,316,271, 2,336,434 and 2,413,907 and US Patents 2,273,780, 2,375,853, 2,388,614, 2,454,547, 3,206,462, 2,261,002, 2,271,378, 3,874,870, 4,001,432, 3,929,990, 3,966,904, 4,005,193, 4,025,617, 4,025,627, 4,025,653, 4,026,945 and 4,027,020.

(11) polymers of poly(quaternary ammonium) composed of units of formula (VIII):

$$\frac{R_{18}}{X-1} = \frac{R_{18}}{N+-(CH_2)r} - NH-CO-(CH_2)q - CO-NH-(CH_2)s - \frac{R_{20}}{N+-A-R_{21}}$$
(VIII)

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in which formula:

 $R_{18}$ ,  $R_{19}$ ,  $R_{20}$  and  $R_{21}$ , which are identical or different, represent a hydrogen atom or a methyl, ethyl, propyl,  $\beta$ -hydroxyethyl,  $\beta$ -hydroxypropyl or -CH2CH2(OCH2CH2)pOH radical,

where p is equal to 0 or to an integer of between 1 and 6, with the proviso that  $R_{18}$ ,  $R_{19}$ ,  $R_{20}$  and  $R_{21}$  do not simultaneously represent a hydrogen atom,

r and s, which are identical or different, are integers of between 1 and 6,

q is equal to 0 or to an integer of between 1 and 34,

X denotes a halogen atom,

A denotes a radical from a dihalide or preferably represents  $-CH_2-CH_2-O-CH_2-CH_2-$ .

Such compounds are disclosed in particular in Patent Application EP-A-122,324.

Mention may be made among these, for example, of the products "Mirapol A 15", "Mirapol $^{\scriptsize \$}$  AD1",

- 5 "Mirapol $^{\$}$  AZ1" and "Mirapol $^{\$}$  175", sold by the company Miranol.
  - (12) homopolymers or copolymers derived from acrylic or methacrylic acids and comprising units:

in which the  $R_{22}$  groups independently denote H or  $CH_3$ , the Al groups independently denote a linear or branched alkyl group of 1 to 6 carbon atoms or a hydroxyalkyl group of 1 to 4 carbon atoms,

the  $R_{23}$ ,  $R_{24}$  and  $R_{25}$  groups, which are identical or different, independently denote an alkyl group of 1 to 18 carbon atoms or a benzyl radical,

the  $R_{26}$  and  $R_{27}$  groups represent a hydrogen atom or an alkyl group of 1 to 6 carbon atoms,

 $X_2^-$  denotes an anion, for example methyl

20 sulphate or halide, such as chloride or bromide.

The comonomer or comonomers which can be used in the preparation of the corresponding copolymers

belong to the family of acrylamides, methacrylamides, diacetone acrylamides, acrylamides and methacrylamides substituted at the nitrogen by lower alkyl, alkyl esters, of acrylic or methacrylic acids, vinyl-

- 5 pyrrolidone or vinyl esters.
  - (13) quaternary polymers of vinylpyrrolidone and vinylimidizole, such as, for example, the products sold under the names Luviquat<sup>®</sup> FC 905, FC 550 and FC 370 by the Company B.A.S.F.
- 10 (14) polyamines, such as Polyquart® H sold by Henkel, referenced under the name "Polyethylene Glycol (15) Tallow Polyamine" in the CTFA dictionary.
  - (15) crosslinked polymers of methacryloyloxyethyltrimethylammonium salt (for example chloride), such as the
- polymers obtained by homopolymerization of dimethylaminoethyl methacrylate quaternized by methyl chloride or by copolymerization of acrylamide with dimethylaminoethyl methacrylate quaternized by methyl chloride, the homo- or copolymerization being followed
- by a crosslinking by a compound possessing olefinic unsaturation, in particular methylenebisacrylamide or pentaerythritol methacrylate. Use may more particularly be made of a crosslinked acrylamide/methacryloyloxyethyltrimethylammonium chloride (20/80 by weight)
- 25 copolymer in the form of a dispersion comprising 50% by weight of the said copolymer in mineral oil. This dispersion is sold under the name of "Salcare® SC 92" by the Company Allied Colloids. Use may also be made of

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a crosslinked homopolymer of methacryloyloxyethyltrimethylammonium chloride comprising approximately 50% by
weight of the homopolymer in mineral oil. This
dispersion is sold under the name of "Salcare® SC 95"
by the Company Allied Colloids.

Other cationic polymers which can be used in the context of the invention are polyalkyleneimines, in particular polyethyleneimines, polymers comprising vinylpyridine or vinylpyridinium units, condensates of polyamines and of epichlorohydrin, quaternary polyureylenes and chitin derivatives.

According to the invention, use may more particularly be made of polymers chosen from Mirapol, the compound of formula (VII) in which  $R_{13}$ ,  $R_{14}$ ,  $R_{15}$  and  $R_{16}$  represent the methyl radical, Al represents the radical of formula  $-(CH_2)_3-$  and Bl represents the radical of formula  $-(CH_2)_6-$  and  $X^-$  represents the chloride anion and the compound of formula (VII) in which  $R_{13}$  and  $R_{14}$  represent the ethyl radical,  $R_{15}$  and  $R_{16}$  represent the methyl radical, Al and Bl represent the radical of formula  $-(CH_2)_3-$  and  $X^-$  represents the bromide anion.

Among all the cationic polymers capable of being used in the context of the present invention, it is preferable to employ quaternary cellulose ether derivatives, such as the products sold under the name "JR® 400" by the Company Union Carbide Corporation, cyclopolymers, in particular the homopolymers of

diallydimethylammonium chloride sold under the name "Merquat® 100" and its homologues of lower molecular weight, and the copolymers of diallyldimethylammonium chloride and of acrylamide sold under the names "Merquat® 550" and "Merquat S" by the Company Merck, or cationic polysaccharides and more particularly the guar gum modified by 2,3-epoxypropyltrimethylammonium chloride sold under the name "Jaguar® C13S" by the Company Meyhall.

According to the invention, the cationic polymer or polymers can represent from 0.001% to 10% by weight, preferably from 0.005% to 5% by weight and more preferably still from 0.01% to 3% by weight of the total weight of the final composition.

## 15 (ii) Amine-comprising silicones

# (1) Amine-comprising silicones

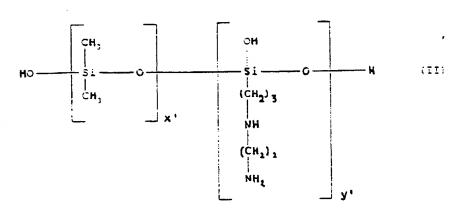
The amine-comprising silicone according to the invention have a weight-average molecular mass of between 11,000 and 25,000.

According to the invention, the term "amine-comprising silicone" denotes any silicone comprising at least one primary, secondary or tertiary amine or one quaternary ammonium group.

Mention may thus be made of:

(a) polysiloxanes called "amodimethicone" in the CTFA dictionary (4th ed., 1991) and corresponding to the formula:

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in which x' and y' are integers which depend on the weight-average molecular mass, such that the said molecular mass is between 11,000 and 25,000,

(b) polysiloxanes called "amodimethicone" in the CTFA dictionary (7th ed., 1997) and corresponding to the formula:

$$R = \begin{bmatrix} CH_3 & & & & \\ & & & \\ Si & & & \\ & CH_3 & & \\ & & CH_2 \end{pmatrix}_3 = \begin{bmatrix} CH_3 & & \\ & & \\ Si & & \\ & CH_2 \end{pmatrix}_2 = \begin{bmatrix} CH_3 & & \\ &$$

in which R denotes OH or methyl,

10 the weight-average molecular mass being between 11,000 and 25,000.

When these amine-comprising silicones are employed, a particularly advantageous embodiment is their use in the form of an oil-in-water emulsion. The surfactants can be of any nature but are preferably cationic and/or nonionic. Use may be made, for example,

of the product sold under the name "Silsoft TP515 Silicone Emulsion" by the Company OSI, which comprises, in addition to amodimethicone, a cationic surfactant comprising a mixture of products corresponding to the formula

R<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CL 
$$\odot$$

in which  $R_9$  denotes alkenyl and/or alkyl radicals having from 12 to 20 carbon atoms and preferably 16 carbon atoms,

in combination with a nonionic surfactant known under the name " $C_{11}$ - $C_{15}$  Pareth-15", which is a mixture of  $C_{11}$ - $C_{15}$  fatty alcohols polyoxyethylenated on average with 15 mol of ethylene oxide.

The mean size of the silicone particles in

the emulsion is generally between 30 nm and 2 microns,

preferably between 0.1 and 0.5 microns and more

particularly between 0.1 and 0.3 microns.

The weight-average molecular masses of these

amine-comprising silicones are measured by gel permeation chromatography (GPC) at room temperature as polystyrene equivalent. The columns used are  $\mu$  styragel columns. The eluent is THF and the flow rate is 1 ml/min. 200  $\mu$ l of a 0.5% by weight solution of silicone in THF are injected. Detection is carried out by refractrometry and UVmetry.

The compositions in accordance with the invention comprise the amine-comprising silicones defined above at contents by weight which can be between 0.05% and 10%, preferably between 0.1% and 7% and more preferably still between 0.2% and 5% with respect to the total weight of the composition.

The vehicle, or carrier, of the detergent compositions according to the invention is preferably water or an aqueous/alcoholic solution of a lower alcohol, such as ethanol, isopropanol or butanol.

The detergent compositions according to the invention exhibit a final pH generally of between 3 and 10. This pH is preferably between 5 and 8. The adjustment of the pH to the desired value can be carried out conventionally by addition of a base (organic or inorganic) to the composition, for example aqueous ammonia, sodium hydroxide or a primary, secondary or tertiary (poly) amine, such as monoethanolamine, diethanolamine, triethanolamine,

isopropanolamine or 1,3-propanediamine, or alternatively by addition of an acid, preferably a carboxylic acid, such as, for example, citric acid.

The detergent compositions according to the invention can, of course, additionally comprise all the usual adjuvants, such as, for example, fragrances, preservatives, sequestering agents, thickeners, softeners, foam-modifying agents, colorants, pearlescent agents, moisturizing agents, antidandruff

or antiseborrhoeic agents, vitamins, silicone or non-silicone sunscreens, suspending agents, proteins, silicones, ceramides, pseudoceramides, fatty acids with linear or branched  $C_{16}$ - $C_{40}$  chains, hydroxy acids, electrolytes, polymers and others.

Of course, a person skilled in the art will take care to choose this or these possible additional compounds and/or their amounts so that the advantageous properties intrinsically attached to the combination

(washing base + cationic polymer + a specific silicone) in accordance with the invention are not, or not substantially, detrimentally affected by the envisaged addition or additions.

These compositions can be provided in the

15 form of more or less thickened liquids, of creams or of
gel and they are mainly suitable for washing, caring
for and/or styling the hair.

When the compositions in accordance with the invention are employed as conventional shampoos, they

20 are simply applied to wet hair and the foam generated by massaging or rubbing with the hands is then removed, after an optional period of rest, by rinsing with water, it being possible for the operation to be repeated one or more times.

Another subject-matter of the invention is a process for washing and for conditioning keratinous substances, such as the hair, which consists in applying, to the said wetted fibres, an effective

amount of a composition as defined above and in then rinsing with water, after an optional period of rest.

As indicated above, the compositions in accordance with the invention confer on the hair, after rinsing, a notable styling effect which is expressed in particular by an ease of styling and of form retention, as well as a contribution of body and of lightness, which are markedly improved.

A concrete but in no way limiting example 10 illustrating the invention will now be given.

#### **EXAMPLE**

Two shampoo compositions were prepared, one in accordance with the invention (composition A) and the other comparative (composition B):

	<u>A</u>	<u>B</u>
	Invention	Comparative
- Sodium lauryl ether	14 g AM	14 g AM
sulphate (70/30 C12/C14)		
comprising 2.2 mol of		
ethylene oxide as an aqueous		
solution comprising 28% of AM		
(AM = active material)		
- Miranol C2M Conc(*)	3.6 g AM	3.6 g AM
- Cationic polymer (**)	0.2 g	0.2 g
- Amine-comprising silicone	2.45 g AM	
according to the invention		•
(***)		
- Amine-comprising silicone		2.45 g
(****)		
- Mixture of 1-	2.5 g	2.5 g
(hexadecyloxy)octadodecanol		
and of cetyl alcohol		
- Monoisopropanolamide of	0.8 g	0.8 g
copra acids		
- Citric acid, q.s. pH	5	5
- Demineralized water, q.s.	100 g	100 g

<sup>(\*):</sup> Sodium cocoamidoethyl(N-hydroxyethyl-N-carboxymethyl)glycinate, sold by Rhône-Poulenc

- (\*\*): Guar gum modified by 2,3-epoxypropyltrimethylammonium chloride, sold under the name Jaguar® C13 S by the company Rhône-Poulenc
- (\*\*\*): Amodimethicone with a weight-average molecular mass of approximately 15,000, sold as a cationic emulsion with an active material content of 35% under the name Silsoft® TP515 Silicone Emulsion" by the Company OSI.
- (\*\*\*\*): Amodimethicone with a weight-average molecular mass of approximately 50,000, sold as a cationic emulsion with an active material content of 35% under the name Fluid DC 939 by the Company Dow Corning.

Shampooing is carried out by applying

15 approximately 12 g of the composition A to sensitive hair which has been wetted beforehand. The shampoo is made to foam and then copious rinsing is carried out with water.

The same procedure is carried out as above with the comparative composition B.

A panel of experts evaluates the disentangling of the dried hair and the softness, the body, the feel and the sleekness of the dried hair.

All the experts indicate a marked improvement
in these properties for the hair treated with the
composition A according to the invention.